

Maciej KOZAK¹, Ludwik DOMKA², Andrzej SKRZYPCZAK³,

ADSORPTION OF THE QUATERNANRY AMMONIUM SALTS ON BENTONITE

Received March 5, 2002; reviewed and accepted May 15, 2002

Sodium bentonite was subjected to the effect of two new homologue series of chlorides (alcoxymethyl) dimethyloctylammonium chlorides and 3-alcoxymethyl-1-octylimidazole chlorides with the hydrophobic substituents of the same length. Morphology of the obtained modified bentonite was studied under scanning electron microscope [SEM] and the degree of adsorption of the ammonium salts was determined by two-phase titration. The results allowed an assessment of the influence of the length of the hydrophobic substituents and the site of the quaternary nitrogen atom on the adsorption of chlorides.

Key words: bentonite, surface modification, quaternary ammonium salts

INTRODUCTION

Bentonites belong to a group of clay minerals formed as a result of the process of weathering of volcanic ashes. The main component of bentonite (over 60%) is montmorillonite a representative of stratiform silicates containing some amounts of quartz, and small admixtures of illite, calcite, mica, chlorites and undecomposed grains of volcanic glass. Montmorillonite from the group of smectites is a representative of the 2:1 type stratiform silicates. It is built of packets of two tetrahedral silicate layers and an octahedral (metalhydroxyl) with adjacent margins. As a result of isomorphous replacement of clay from the octahedral layer by cations of lower valence an excessive negative charge appears on the packet surface. This negative charge is compensated by the adsorption of cations in the interpacket space.

¹ Adam Mickiewicz University, School of Physics, Poznan

² Center of Technology, School of Chemistry, Adam Mickiewicz University, Poznan

³ Poznan University of Technology, School of Chemical Technology, Poznan

Therefore, the most general classification of bentonites is based on the type of cations dominant in the interpacket space – sodium, calcium or rarely magnesium (Van Olphen, 1977; Worrall, 1986).

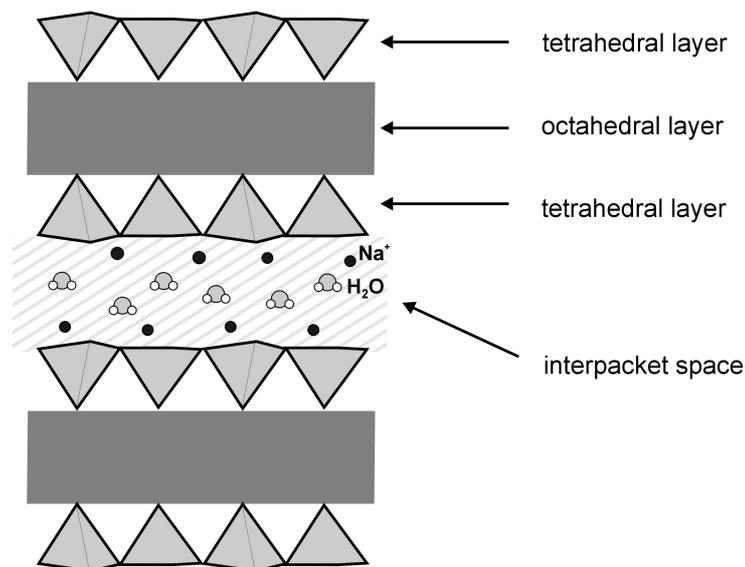


Fig. 1. Schematic representation of montmorillonite structure

The bentonites of high content of sodium montmorillonite reveal an ability to adsorb water in the interpacket space. This ability is very interesting from the point of view of technological applications. Water penetrating among the silicate layers forms layers of about 0.3 nm in thickness, consequently bentonite is capable of adsorbing the mass of water 5 times greater than its own mass. The layer of hydrated bentonite makes a compact barrier for the flow of liquid. Therefore, bentonite is often used in construction of sealing layers, geomembranes or in drilling technology. According to a similar mechanism other solvents, surfactant solutions or polymers may be adsorbed in bentonites. Investigation of this phenomenon is particularly important because of the promising possibility of application of the modified bentonite or pure montmorillonite in polymer technology for preparation of new nanocomposite systems characterised by unique mechanical properties (LeBaron et al., 1999; Alexandre and Dubois, 2000).

This study was meant as an attempt at determination of the adsorption properties of bentonite with respect to quaternary ammonium salts. Adsorption of these compounds on the surface of silica has been well recognised (Drach et al., 1998; Esumi et al., 1996), but adsorption of quaternary ammonium salts on bentonite has not been the subject of interest of many authors. The results of this study were meant to provide information on the adsorption of the salts on the properties of the modified bentonite.

Two new homologous series of chlorides have been chosen for the study: (alcoxymethyl)dimethyloctylammonium chlorides and 3-alcoxymethyl-1-octylimidazole chlorides with the hydrophobic substituents of the same length differing in the site of appearance of the positive charge. In the compounds of the first series the positive charge is localised at the ammonium nitrogen atom, while in the second it is delocalised on the imidazole ring. The aim of the study was to determine the influence of the hydrophobic substituents length and the site of the quaternary nitrogen atom (with positive charge) on the process of adsorption in bentonite.

MATERIALS AND METHODS

REAGENTS

Powdered bentonite was purchased at the Fisher Scientific, Great Britain. The chlorides used (alcoxymethyl)dimethyloctylammonium and 3-alcoxymethyl-1-octylimidazole chlorides were obtained in the reaction of a proper chloromethylalkil ether with N,N-dimethyloctylamine or 1-octylimidazole according to the procedure described by Pernak et al. (1987) and Skrzypczak et al. (1997).

Table 1. List of the compounds synthesised

No.	Compound Name	Reaction yield wt.
1	(butoxymethyl)dimethyloctylammonium chloride	95,3%
2	dimethyl(hexyloxymethyl)octylammonium chloride	92,1%
3	dimethyloctyl(octyloxymethyl)ammonium chloride	93,6%
4	(decyloxymethyl)dimethyloctylammonium chloride	90,4%
5	dimethyl(dodecyloxymethyl)octylammonium chloride	88,3%
6	3-butoxymethyl-1-octylimidazole chloride	97,5%
7	3-hexyloxymethyl-1-octylimidazole chloride	94,6%
8	1-octyl-3-oktyloxymethylimidazole chloride	86,5%
9	3-decyloxymethyl-1-octylimidazole chloride	89,9%
10	3-dodecyloxymethyl-1-octylimidazole chloride	85,7%

After synthesis, isolation and purification procedures the purity of each compound was checked by thin layer chromatography.

MODIFICATION OF THE BENTONITE SURFACE

The study was performed with the use of water solutions of the quaternary ammonium salts of the concentration of 2 g/dm³. To portions of 20 cm³ of a given solution of the quaternary salt the weighted portions of bentonite of 0.02g, 0.04g, 0.06g, 0.08g, 0.10g were added. The solution with a given portion of bentonite was

intensely stirred for 20 min and filtered off through a qualitative filter at a moderate rate of filtration. The precipitate was washed with three portions of distilled water, afterwards left for further analysis. The precipitate was subjected to morphological examination under a scanning electron microscope.

SCANNING ELECTRON MICROSCOPY SEM

Morphology of the samples was examined by scanning electron microscopy (SEM-515, Philips). The powdered sample, intended for the studies, was dispersed in *t*-butanol and, following sedimentation on a microscope holder, it was coated with gold in an ionisation chamber. The typical magnification ratio was 2,500 \times .

TWO-PHASE TITRATION

The filtrate was tested for the presence of the cation-active substance according to the procedure recommended by the Polish standards PN-87/C-04818. The titration was performed in a two-phase water-chloroform system by the solution of sodium dodecyl sulphate in the presence of a mixed indicator composed of a mixture of a cationic indicator (dimidiowy bromide) and an anionic indicator (disulphine blue). The anionic salt reacts with the mixed indicator forming a salt, which dissolves in chloroform giving a specific blue colour. Upon titration, sodium dodecyl sulphate added displaces the anionic indicator from the salt, which changes the colour of the chloroform layer into pink.

RESULTS AND DISCUSSION

The morphology of the unmodified bentonite is shown in Fig. 1, while Fig. 2 shows the morphology of the 0.02 g bentonite sample after adsorption of (butoxymethyl) dimethylctylammonium chloride. A comparison of the photographs proves that the adsorption of the chloride did not cause an increase of the degree of agglomeration of bentonite particles. The sample after modification reveals some prevalence of the fraction of greater particles but also a better equalisation.

Figures 4 and 5 present the loss of ammonium and imidazole chlorides studied from the solution as a function of the bentonite concentration. The results of two-phase titration presented in Fig. 4 and 5 indicate that the adsorption of the compounds studied on bentonite is not a linear process. At the first stage, so for the weighted portion of 0.02g bentonite, a significant loss of a given quaternary salt from the solution is observed. When a multiplied portion is used the adsorption grows systematically (for almost all compounds) but usually is by one order of magnitude lower than that for the portion of 0.02g of bentonite. These data suggest that the description of the process of adsorption of the quaternary salts studied from water solutions on the surface of bentonite should take into regard the surface activity properties of these compounds.

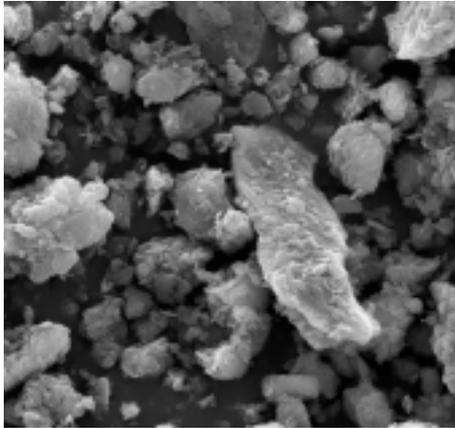


Fig. 2. Standard bentonite (SEM microphotograph, 2,500 x magnification)

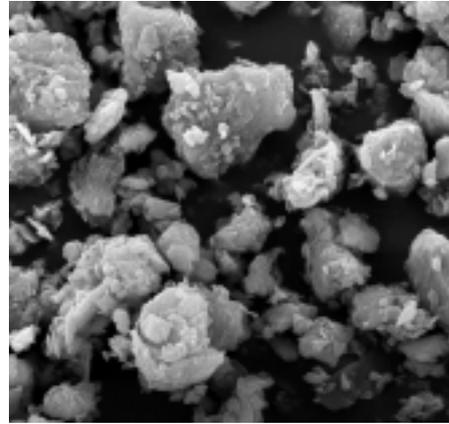


Fig. 3. Bentonite after adsorption of (butoxymethyl)dimethyloctylammonium chloride (on 0.02 g bentonite) (SEM microphotograph, 2,500 x magnification)

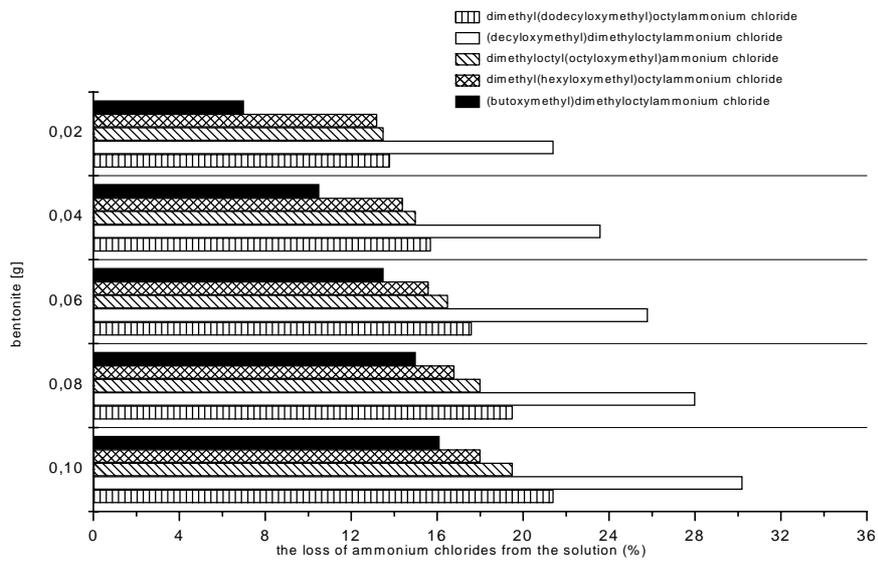


Fig. 4. The loss of ammonium chlorides from the water solution as a function of the bentonite added

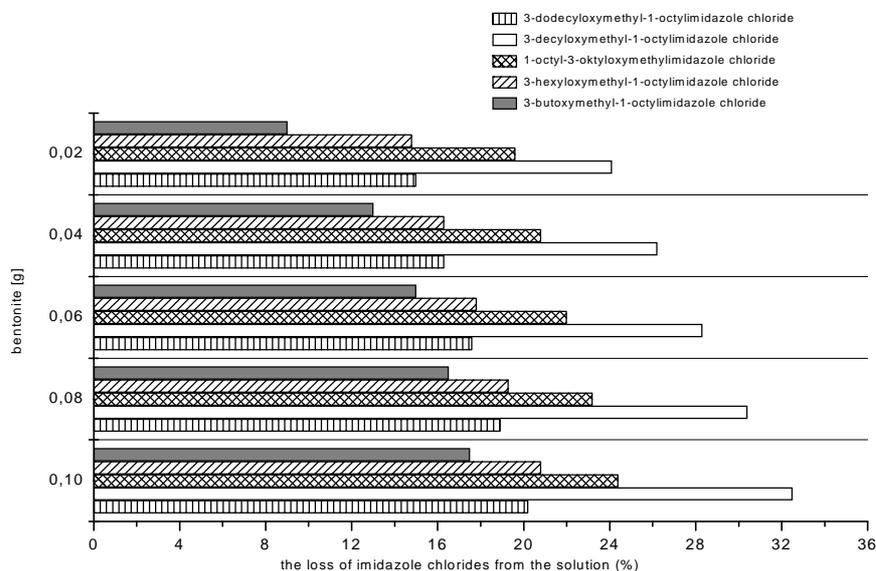


Fig. 5. The loss of imidazole chlorides from the water solution as a function of the bentonite added

Analysis of the loss of ammonium and imidazole chlorides in the solution, has shown that it becomes more pronounced with increasing length of the substituent (from butoxymethyl to decyloxymethyl). The smallest loss of the quaternary salt in the solution (relative to the weighted portion of 0.1 g of bentonite) was observed for (butoxymethyl)dimethyloctylammonium chloride (16.1 %) and 3-butoxymethyl-1-octylimidazole chloride (17 %), while the greatest for (decyloxymethyl)-dimethyloctylammonium chloride (30.2 %) and 3-decyloxymethyl-1-octylimidazole chloride (32.5 %). For the longest substituent (dodecyloxymethyl) a deviation from the above rule was noted and the values of the loss of dimethyl(dodecyloxymethyl) octylammonium chloride and 3-dodecyloxymethyl-1-octylimidazole chloride were 21.4 % and 20.2 %, respectively.

A probable mechanism of adsorption of surfactants on the surface of bentonite (Fig. 6) dependent on the surfactant concentration was proposed by Alemdar et al. (2000) for adsorption of cetyltrimethylammonium bromide (CTAB) and distearyldimethylammonium chloride (DDAC) on the surface of sodium and calcium bentonite. This mechanism (Fig. 6) involving adsorption on a single or double layer depending on the bentonite concentration, is also valid for the quaternary salts studied. A comparison of the percent loss of the chlorides from the two homologue series from water solutions as a result of adsorption on bentonite brings about the information on the effect of localisation of the positive charge on the character of the adsorption studied.

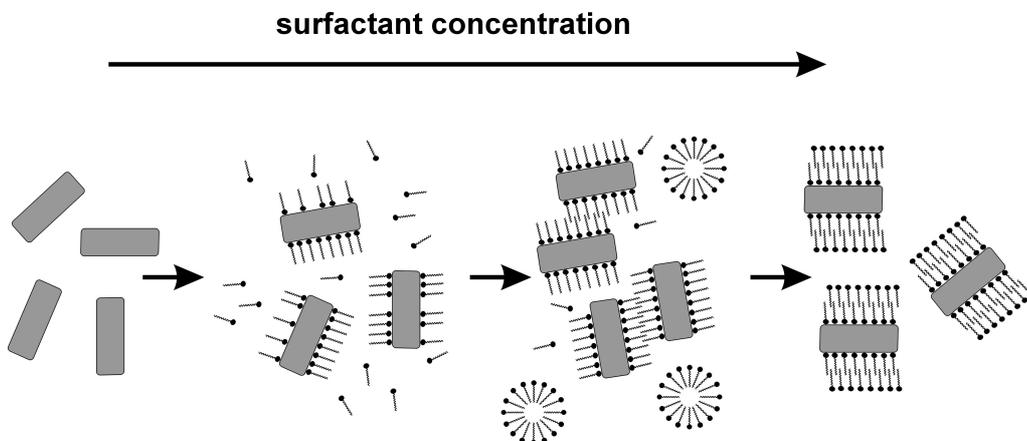


Fig. 6. Schematic representation of adsorption of cationic surfactants on bentonite as a function of surfactant concentration (after Alemdar et al. 2000)

A similar nonlinear character of surfactants adsorption has also been observed by other authors in adsorption of sodium dodecylbenzene sulfonate on organophilic bentonites (Rodríguez-Sarmiento and Pinzon-Bello, 2001) and in modification of bentonite using nonionic surfactants (Shen, 2001).

The compounds with the imidazole core in which the positive charge is localised on the imidazole ring are adsorbed to a degree by a few percent greater than those in which the positive charge is localised on a specific nitrogen atom (ammonium compounds).

ACKNOWLEDGMENT

The work was supported by intercollegiate (UAM/AE) grant. The authors would like to thank Rectors of Adam Mickiewicz University (Poznań) as well as Poznań University of Economics for generous support.

REFERENCES

- ALEMDAR A., ATICI O., GÜNGÖR N. (2000) *The influence of cationic surfactants on rheological properties of bentonite-water systems*. Materials Letters, Vol. 43, 57.
- ALEXANDRE M., DUBOIS P. (2000) *Polymer-layered nanocomposites: preparation, properties and uses of a new class of materials*. Material Science and Engineering, Vol. 28, 1.
- DRACH M., ŁAJTAR L., NARKIEWICZ-MICHAŁEK J., RUDZIŃSKI W., ZAJĄC J. (1998) *Adsorption of cationic surfactants on hydrophilic silica: effects of surface energetic heterogeneity*, Colloids and Surfaces, Vol. 145, 245.
- ESUMI K., GOINO M., KOIDE Y. (1996) *Adsorption and adsolubilization by monomeric, dimeric, or trimeric quaternary ammonium surfactant at silica/water interface*, J. Coll. and Int.Sci., Vol. 183, 539.
- LeBARON P.C., WANG Z., PINNAVAIA T.J. (1999), *Polymer-layered silicate nanocomposites: an overview*. Applied Clay Sciences Vpl 15, 11.
- PERNAK J., KRYSIŃSKI J., SKRZYPCZAK A. (1987), Tenside Surfactans Detergents, Vol. 24, 276.

- RODRIGUEZ-SARMIENTO D.C., PINZON-BELLO J.A. (2001), *Adsorption of sodium dodecylbenzene sulfonate on organophilic bentonites*. Appl. Clay Sci. Vol. 18, 173.
- SKRZYPCZAK A., BRYCKI B., MIRSKA I., PERNAK J. (1997). *Synthesis and antimicrobial activities of new quats*, Eur. J. Med. Chem., Vol. 32, 661.
- SHEN Y.H. (2001), *Preparations of organobentonite using non-ionic surfactants*. Chemosphere Vol. 44, 989.
- WORRAL E. (1986), *Clays and Ceramic Raw Materials*, Elsevier, London.
- VAN OLPHEN H. (1977), *Clay Colloid Chemistry*, Willey, New York.

Kozak M., Domka L., Skrzypczak A., *Adsorpcja czwartorzędowych soli amoniowych na bentonicie*, Fizykochemiczne Problemy Mineralurgii, 36, 2002, 299-306 (w jęz. ang.).

W ramach prezentowanych badań poddaliśmy bentonit sodowy działaniu dwóch nowych szeregów homologicznych chlorków (alkoksymetylo)dimetylo-oktyloamoniowych oraz chlorków 3-alkoksymetylo-1-oktyloimidazoliowych o identycznej długości analogicznych podstawników hydrofobowych. Przeprowadziliśmy analizę morfologii zmodyfikowanego bentonitu z użyciem skaningowej mikroskopii elektronowej oraz stopnia adsorpcji soli amoniowej przy pomocy miareczkowania dwufazowego. Uzyskane wyniki pozwoliły określić wpływ długości podstawników hydrofobowych oraz miejsca, gdzie występuje czwartorzędowy atom azotu, na proces adsorpcji chlorków.